Applied Surface Science 392 (2017) 514–522

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Surfactant-free synthesis of hierarchical niobic acid microflowers assembled from ultrathin nanosheets with efficient photoactivities

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ARTICLE INFO

Article history:
Received 16 July 2016
Received in revised form 3 September 2016
Accepted 19 September 2016
Available online 19 September 2016

Keywords:
Hierarchical microflower
Nanosheet-assemble
Niobic acid
Niobium pentoxide

ABSTRACT

Hierarchical niobic acid ($Nb_2O_5{\cdot}nH_2O$) microflowers are synthesized by a surfactant-free hydrothermal approach. The three-dimensional microflowers are assembled from two-dimensional ultrathin nanosheets with thickness of ~5 nm. Using rhodamine B as a probe, the $Nb_2O_5{\cdot}nH_2O$ microflowers exhibit high photocatalytic activity under UV light irradiation. Furthermore, the $Nb_2O_5{\cdot}nH_2O$ microflowers are easily converted to niobium pentoxide without significant structural alteration.

1. Introduction

In the past decades, rational design and controllable synthesis of functional semiconducting materials with desired nano/microstructures has received extensive studies for the improved performance in structure-dependent applications [1–4]. In particular, three-dimensional (3D) hierarchical nano/microstructures assembled with low dimensional nanoscale building blocks have attracted increasing interests due to their combinations of the advantages of primary building blocks and the secondary unique 3D architectures [5–7]. To date, many metal oxides with 3D hierarchical structures, such as TiO_2 [8,9], SnO_2 [6], ZnO [7,10], MnO_2 [11,12], NiO [13], and Fe_2O_3 [14] have been synthesized. In general, the fabrication of morphology-controlled nanostructures is carried out by using surfactants as structure-directing agents. However, these additives are often costly and the induced impurities can decrease the activity of as-prepared materials [14]. Thus, it remains challenging but desirable to synthesize 3D hierarchical architectures by a facial organic-free route.

Niobium oxides, mainly including niobic acid (hydrated niobium oxide, $Nb_2O_5{\cdot}nH_2O$) and niobium pentoxide (Nb_2O_5), have been attracted a lot of attentions due to their promising applications in various fields such as photocatalysts [15–18], gas sensors [19,20], photodetectors [16,21], electron field emitters [22], lithium-ion batteries [23–26], dye-sensitized solar cells [27,28], and solid acid catalysts [29,30]. Since the performances of nanomaterials deeply depend on their crystal-structures and apparent-morphologies, a great deal of efforts has been devoted to the dimension design and structure control [31–33]. To date, various niobium oxides nanostructures include nanowires [22,34,35], nanobelts [21,36], nanorods [37–39], nanotubes [40–42], nanofibers [43], nanoplates [16,44], and nanosheets [26,29] have been obtained during the past few years. Furthermore, these low dimensional nanostructures could be self-assembled into 3D hierarchical architectures to gain extra physiochemical properties. For example, Zhang and co-workers fabricated 3D $Nb_3O_7(OH)$ and Nb_2O_5 superstructures assembled with one-dimensional (1D) nanowire arrays by a hydrothermal process [45]. Guo et al. synthesized 3D hierarchical flower-like Nb_2O_5 microspheres composed of two-dimensional (2D) nanosheets via a hydrothermal approach

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http://dx.doi.org/10.1016/j.apsusc.2016.09.085
0169-4332/

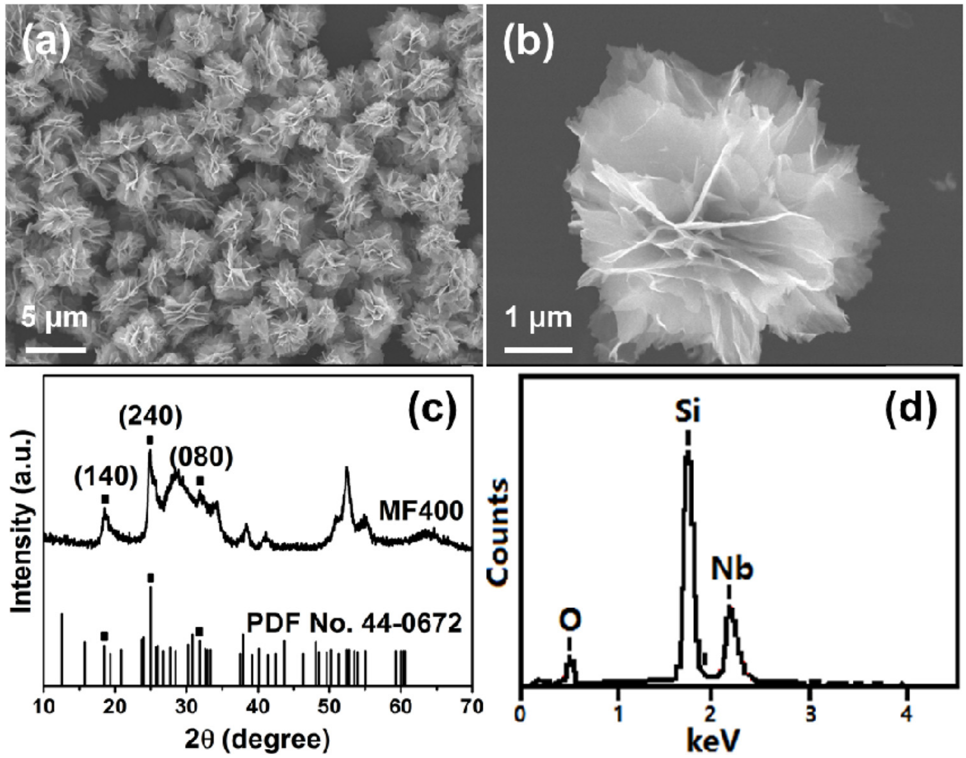

Fig. 1. (a, b) FESEM images, (c) XRD pattern, and (d) EDX spectroscopic analysis of the as-prepared MF400 sample. The Si signal arises from the used basis.

with hexamethylenetetramine [46]. However, it is still desirable to fabricate 3D hierarchical niobium oxides structures by a cheaper and greener route.

Herein, we report the synthesis of 3D $Nb_2O_5{\cdot}nH_2O$ microflowers assembled from ultrathin nanosheets by an organic-free method. The photocatalytic activity of as-prepared sample was evaluated by the photodegradation of rhodamine B (RhB) solution. The as-prepared microflowers exhibited higher RhB removal rate compared with commercial P25 TiO_2. Additionally, the crystal phase of this microflower can be easily transformed from $Nb_2O_5{\cdot}nH_2O$ to Nb_2O_5 by calcination.

2. Experimental

2.1. Materials

The materials used in this work consist of niobium pentachloride ($NbCl_5$), 25 wt% ammonium hydroxide solution, hydrochloric acid (37%, HCl) solution, absolute ethanol, and ethanol. All chemicals were used as received without further purification.

2.2. Synthesis of niobium oxide nanostructures

$Nb_2O_5{\cdot}nH_2O$ microflowers were synthesized through a modified hydrothermal method [29]. In a typical synthesis, 200 mg (0.74 mmol) $NbCl_5$ was dissolved in 2 mL absolute ethanol. Under vigorous stirring, 8.5 mL deionized (DI) water and 1.5 mL ammonium hydroxide solution were added into the $NbCl_5$ ethanol solution, respectively. After being stirred for 2 h at room temperature, the white precipitate was separated by centrifugation and ultrasonically dispersed in 28 mL DI water. The suspension was sealed into a Teflon-lined stainless-steel autoclave (50 mL capacity) at 200 °C for 24 h. After the autoclave was cooled to room temperature naturally, the products were washed by DI water and dried in vacuum at 60 °C overnight.

The as-prepared microflowers are denoted as MF. The MF samples were annealed for 2 h in air at 400 °C to remove adsorbed residuals, and 600 °C to convert to Nb_2O_5 phase; they are denoted as MF400 and MF600, respectively. The products synthesized under the same procedure but with different hydrothermal reaction time are denoted as NbO-x, where x stands for the hydrothermal reaction time.

Nb_2O_5 nanoneedles were synthesized via the same process except for tuning the pH value of the suspension to 6 via dropping of HCl solution before hydrothermal reaction. The nanoneedles are denoted as NN.

2.3. Characterization

The morphology and structure of the samples were determined by field-emission scanning electron microscopy (FESEM, JEOL 6701F), transmission electron microscopy (TEM, JEOL 2010) and corresponding selected area electron diffraction (SAED). The elemental compositions of the samples were analyzed with energy-dispersive X-ray spectroscopy (EDX) attached to the FESEM instrument. The X-ray diffraction (XRD) patterns were obtained on a Rigaku D/MAX 2500 diffractometer with Cu Kα radiation. The nitrogen adsorption isotherms were performed over niobium oxide samples at 77 K on an automated gas sorption analyzer (Quantachrome instruments autosob iQ_2). Samples were degassed at 150 °C for 3 h before measurements. The specific surface area and pore size distribution were calculated by the Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halender (BJH) methods, respectively. The optical properties of the samples were characterized by UV–vis diffuse reflectance spectra (UV–vis DRS) at room temperature on a UV–vis spectrometer (Shimadzu UV-2600) with barium sulfate as the reference. The Raman spectra were collected by a Raman microscope system (Thermo Scientific DXR) with laser excitation wavelength of 532 nm.